Effects of magnetic impurity plus association on the Knight shifts in liquid Bi–In–Ni alloys

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Abstract. In liquid Bi–In–Ni alloys the dependences of the Bi Knight shift $K(\mathrm{Bi})$ and the In Knight shift, $K(\mathrm{In})$, respectively, on the concentrations c_{Ni}, c_{Bi} and c_{In} have been measured, as well as the linewidths. The concentration ranges were $c_{\mathrm{Ni}} = 0$–0.20, $c_{\mathrm{Bi}} = 0$–1 and $c_{\mathrm{In}} = 0$–1, at temperatures of 1000–1300 K. The addition of Ni increases K by $\Gamma = c_{\mathrm{Ni}}^{-1} \cdot \mathrm{d}K/K \simeq 1$ for In, and $\Gamma \simeq 0.5$ for Bi. The considerable non-linear changes in $K(\mathrm{Bi})$ and $K(\mathrm{In})$ with $c_{\mathrm{Bi}}/c_{\mathrm{In}}$ that are known to occur in the binary Bi–In system retain their general shapes on addition of Ni. The contribution of Ni d electrons to both Knight shifts has a large term proportional to c_{Ni}^2, which is negative for $K(\mathrm{In})$ and positive for $K(\mathrm{Bi})$. The spin polarisation is evaluated. Changes in K in the ternary liquid alloy are compared with a superposition of the changes known from the binaries; at $c_{\mathrm{Ni}} \simeq 0.20$, deviations occur for $K(\mathrm{In})$.

1. Introduction

Paramagnetic atoms dissolved at a low concentration in metallic liquids induce specific additional Knight shifts on the matrix atoms. Several studies, in particular on Mn, Fe and Co concentrations of a few atomic per cent in liquid Al, Au, Bi, Cu, Ga and Sb [1] have shown that these 3d atoms essentially retain a localised magnetic moment, in accordance with for example susceptibility and Kondo effect behaviour. For the $3\mathrm{d}^9$ atom Ni, however, in liquid In [2] or Bi [3], no local moment survives, again in accordance with susceptibility [4, 5] and the solid alloy properties of Al–Ni, Au–Ni and Cu–Ni (see e.g., [6]). Moreover, the 3d band is close to being filled. This situation suggests a search for the dependence of the Ni magnetic state on the electronic state of the surrounding. The latter can be varied by using an alloy as the matrix. Differences between Ni–In and Ni–Bi, for example, are obvious [2, 3].

Many binary liquid alloys A–B reveal a bonding interaction between partners, which is most directly observable as marked negative enthalpy of mixing ΔH. The phenomenon is usually a corollary of solid stoichiometric compounds $A_\mu B_\nu$. Examples are the III–V systems, among which the case In–Bi shows relatively weak bonding (see e.g., [7]). Besides ΔH the influence of the attractive interaction in the liquid state is also observed—depending on its strength—in the Knight shift [8], the susceptibility, the resistivity, the density, nuclear quadrupolar relaxation [9], and the temperature dependence of the Knight shift [10].

Since the dependence of the Knight shift K of liquid Bi (as well as of liquid In) on

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added Ni has been thoroughly studied [2, 3], and Bi–In shows definite effects of bonding in the liquid state [9], it was interesting to determine experimentally the changes in K for Bi and In in Bi–In liquid alloys on the addition of Ni.

2. Effects of alloying in binary systems

2.1. Knight shift

Knight shifts in liquid alloys have been determined for a large number of cases [1], but to our knowledge no established treatment exists for this problem (see [11–15] and references therein). Here, we shall therefore resort to a few basic and phenomenological concepts. The Knight shift K in a metallic system is considered as the product of an essentially local factor P associated with the probe atom, i.e. the hyperfine field per polarised spin at ε_F, with a factor determined by the surroundings, i.e. the susceptibility of conduction electrons at ε_F. In simple metals [16], only the Fermi contact term of s electrons is present:

$$K_s = (8\pi/3)\chi_s \Omega P_s \tag{1}$$

$$P_s = \langle |\psi(0)|^2 \rangle_{\varepsilon_F} \tag{2}$$

where χ_s is the Pauli spin susceptibility of the s conduction electrons per volume and Ω is the atomic volume. More precisely, an orbital contribution has to be added, especially in p elements, and also a diamagnetic contribution, and correspondingly for χ:

$$K = K_s + K_{orb} + K_{dia} + \dots \qquad \chi = \chi_s + \chi_{orb} + \chi_{dia} + \dots. \tag{3}$$

K_{dia} is usually negligible. In the free-electron approximation, $\chi_s = \mu_B^2 N(\varepsilon_F)$, where $N(\varepsilon_F)$ is the density of states at ε_F (both spin directions). Introducing the core diamagnetic susceptibility, which can here be assumed to be independent of composition and temperature, one has $\chi_{dia} = \chi_{dia}^{core} - \frac{1}{3}\chi_s$. A free-electron picture is certainly not applicable to the present system, as is obvious from the diamagnetic sign of the susceptibility of both pure liquid metals Bi and In. Up to now, attempts to derive a quantitative interpretation of K remain within 10–30%, even for pure liquid In and Bi (see, e.g., the discussions in [3, 4, 35]; new doubts in the conventional starting formula for K (equation (1)) derive from the fact that recent XPS and UPS spectra obtained in [17] ascribe considerable, if not dominating, p character to the electron states near ε_F in elements such as Bi. All the more, one is forced, in a discussion of the differential changes in K on the addition of Ni, or on varying the temperature, to rely on a phenomenological *ansatz*, which is basically the addition of two further terms to equation (3a):

$$K = K_s + K_{orb} + K_{Nid} + K_{Nis}. \tag{4}$$

The average shift induced in Bi or In by the added Ni atoms is supposed to have a conduction-electron-type contribution K_{Nis}, and a contribution K_{Nid} in which the Ni d electrons act directly (probably via overlap) on the In or Bi cell.

The d^9 element Ni, when dissolved in a metallic non-d matrix, does not develop a local moment. Yet the resonance scattering increases $N(\varepsilon_F)$ and, in the Friedel description of virtually bound d states ($l = 2$), the contribution to a local density of states is $N_d(\varepsilon_F) = 2(\pi\Delta_l)^{-1} 2(2l + 1) \sin^2 \eta_l$ with η_2 the d phase shift and Δ_2 the width of the d resonance [18]. The number of electrons in d states is $z_d = (10/\pi)\eta_2$. It may change by electron transfer between Ni and the surrounding matrix. Here the electronegativity difference comes into play.

2.2. Concentration dependence

The magnetic susceptibility of both Bi–Ni [5] and In–Ni [4] show $d\chi/dT > 0$, essentially proving the absence of local Ni moments. Thus the Friedel picture should apply. Filling
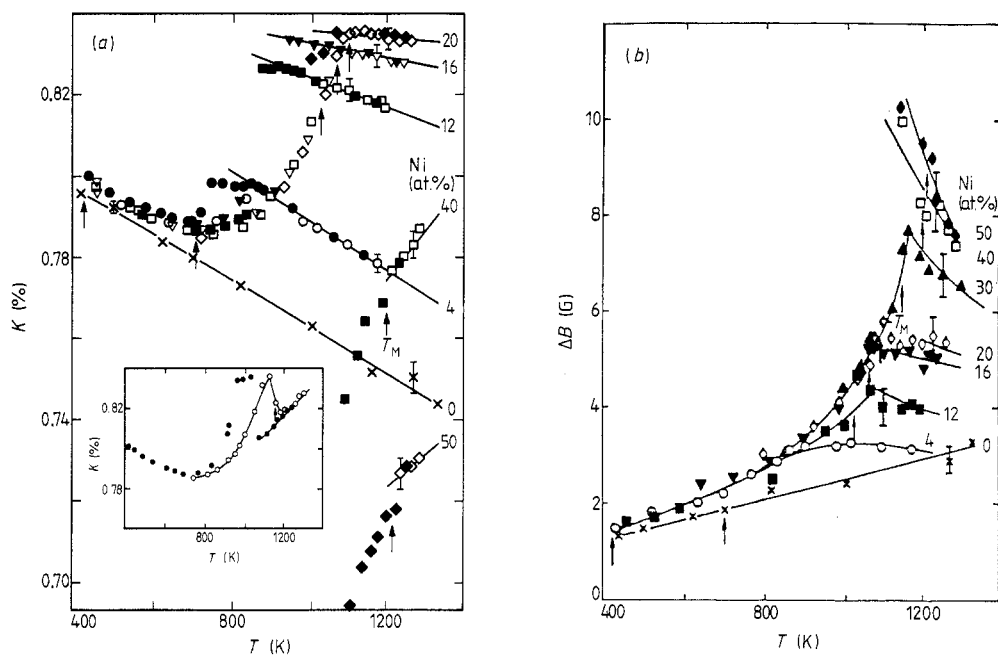
Figure 1. (*a*) Knight shift K for ^{115}In in liquid In–Ni alloys. The arrows indicate melting temperatures T_M:——, lines drawn through the points in the equilibrium liquid state; $\bigcirc$, $\square$, $\triangledown$, $\diamond$, points taken on heating; $\bullet$, $\blacksquare$, $\blacktriangledown$, $\blacklozenge$, points taken on cooling. The inset shows the $c_{Ni} = 0.30$ results separately. (*b*) Linewidth ΔB (10^{-4} T) for ^{115}In in liquid In–Ni alloys. The points have been connected to guide the eye. (Crosses indicate 0% Ni in figures 1–3.)

up of the d band, such as in liquid alloys Ge–Ni [19–21], is claimed to lead finally to the disappearance of any Ni magnetism, but this mechanism apparently does not work in Bi–Ni and In–Ni ($Z_d = 8.6$ in Bi–Ni [5]; $Z_d = 9$ in In–Ni [4]). Figure 1(*a*) presents the Knight shift results for In–Ni.

At higher Ni concentrations in In–Ni, dK/dc turns negative [2], leading to the peculiar behaviour of $K(^{115}\text{In})$ in the alloy $\text{In}_{70}\text{Ni}_{30}$ (inset in figure 1(*a*)). When the alloy is heated, the observed NMR signal corresponds to the composition and temperature of the liquidus line. Therefore, K increases first and then decreases as the concentration $c_{Ni} = 0.20$ is exceeded until, at the liquidus temperature of the $\text{In}_{70}\text{Ni}_{30}$ alloy (1200 K), all Ni is in the liquid state. The slower increase (and later decrease) in K with c_{Ni} can be ascribed to d–d interactions between Ni atoms together with a negative sign of the c_{Ni}^2 contribution to K_{Nid} from In. For Bi in Bi–Ni, however, both linear and quadratic terms contribute with positive sign to K_{Bi} [3].

The inapplicability of the free-electron model is stressed in Bi–In by the deviations from linear interpolations (Bi to In) that occur for $K(\text{Bi})$, $K(\text{In})$, χ and electrical conductivity, at always roughly around In_2Bi [8, 22, 23]. In [8] the slope and plateau-like behaviour of $K(\text{Bi})$ and $K(\text{In})$ were ascribed to the occurrence of an association $\text{Bi} + \text{In} \leftrightarrow \text{InBi}$ in the liquid alloy. The association *ansatz* is now in quantitative use for thermodynamics of liquid alloys (see, e.g., [24]), and it has recently been applied to many metallic liquid alloys, including Bi–In, to explain quadrupolar relaxation rates [9].

Note that the changes induced by the addition of Ni are of the same order of magnitude as those already occurring in the Bi–In system, i.e. $\Delta K/K \simeq 10^{-1}$–$10^{-2}$. To avoid the additional complication from the quadratic term in K_{Nid}, concentrations c_{Ni} were limited in the present work to about 20 at.% or less.

Table 1. Temperature coefficients of Knight shifts for pure liquid metals Bi and In (see § 2.3).

	$d(\ln K)/dT$ $(10^{-5}\,\mathrm{K}^{-1})$	α $(10^{-5}\,\mathrm{K}^{-1})$	$d(\ln \chi)/dT$ $(10^{-5}\,\mathrm{K}^{-1})$	$d[\ln(\Omega P)]/dT$ $(10^{-5}\,\mathrm{K}^{-1})$
Bi	-8.7	11	-3.7	-5.0
In	-7.2	12	-4.02	-3.2

2.3. Temperature dependence

For the pure liquid metals, dK/dT observed at constant pressure [3, 25] is first expected to be mainly a consequence of volume expansion; in the free-electron model,

$$d(\ln K)/dT = d(\ln \chi_s)/dT + d[\ln(\Omega P)]/dT. \tag{5}$$

Introducing the volume dependence $d(\ln \chi_s)/dT$ of the free-electron Pauli susceptibility via the thermal expansion coefficient α explicitly, we show in table 1 that the 'local factor' ΩP contributes a similar temperature dependence as the matrix factor χ_s.

In the liquid Bi–Ni and In–Ni alloys, $dK/dT < 0$ prevails at low c_{Ni} because the matrix effect remains the dominating influence, while $dK/dc_{Ni} > 0$ owing to the K_{Nis} term. For In–Ni [2] at larger c_{Ni} a reversal occurs (see figure 1(a)), with dK/dT becoming positive. This is caused by the negative term (which is proportional to c_{Ni}^2) in K_{Nid}, the magnitude of which decreases with increasing T (because the Ni cell magnetisation decreases). The fact that this particular term is large for $K(\mathrm{In})$ in In–Ni may be due to a stronger In–Ni interaction (several intermetallic phases [26]; larger electronegativity difference), which leads to a stronger transfer of electron spin polarisation from the Ni cell to In, compared with Bi–Ni. In Bi–Ni, dK/dT cannot change sign because the contributions to K_{Nid} which are proportional to c_{Ni} and to c_{Ni}^2 are both positive.

For the liquid Bi–In system, one observes a particularly large dK/dT at $c_{Bi} \simeq 0.50$ [8], which again emphasises the importance of association. Similarly, a strong dK/dT was found for Cu–Ga [10] near a suggestive stoichiometry of Cu_3Ga.

2.4. Linewidths

For Bi–Ni, the linewidth $\Delta B(\mathrm{Bi})$ has been measured and reported in [3]. The width $\Delta B(\mathrm{In})$ for In–Ni [2] is presented in figure 1(b). For liquid In, most of $R = 1/T_1$ is supposedly of magnetic origin; the Korringa rate

$$1/T_1 = (\gamma_n/\gamma_e)^2 (4\pi k_B/\hbar)k(\alpha)K^2 T \tag{6}$$

leads to $T_1(\mathrm{In}) = 0.086 \times 10^{-3}\,\mathrm{s}$ and $T_1(\mathrm{Bi}) = 0.037 \times 10^{-3}\,\mathrm{s}$, i.e. $\Delta B = 1/\sqrt{3}\gamma T_1\pi = 2.3\,\mathrm{G}$ and $\Delta B(\mathrm{Bi}) = 7.3\,\mathrm{G}$ at 1100 K with a typical [27] value $k(\alpha) = 1$ for pure In, and $k(\alpha) = 1.4$ for pure Bi. Equality of T_1 and T_2 is assumed in the liquid.

On the addition of Ni, $K(\mathrm{In})$ changes by about 20% or less, but the linewidth increases by a factor of 3 [2] (a factor of 2 for Bi–Ni [3]). This increase continues even though $K(\mathrm{In})$ bends down at $c_{Ni} > 0.20$, showing that the fluctuations associated with the linear and quadratic terms in K_{Nis} and K_{Nid} are independent. A reason may be the radial dependence of the hyperfine fields induced on In by Ni, which oscillates against r differently for s and d electrons.

The quadrupolar contribution to the linewidth (equation (6)) is probably small for In. The concentration dependence for In–Bi is linear, and $\Delta B(\mathrm{In})$ increases with increasing temperature (from equation (6)), whereas the quadrupolar ΔB_Q would decrease with increasing T and be roughly of shape $c(1 - c)$; also, according to [9], $\Delta B \leqslant 1\,\mathrm{kHz}$. For Bi, however, a contribution ΔB_Q comparable with ΔB_M is obvious from
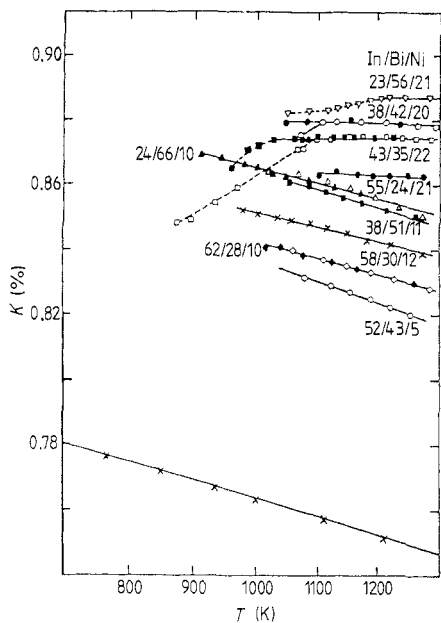
Figure 2. Knight shift K for ^{115}In in liquid Bi–In–Ni alloys. The breaks are due to incipient crystallisation: ———, lines drawn through the points in the equilibrium liquid; $\triangledown$, $\bigcirc$, $\square$, $\triangle$, $\diamond$, temperature raised; $\bullet$, $\blacksquare$, $\blacktriangle$, $\blacklozenge$, temperature decreased; *lowest curve, pure In.*
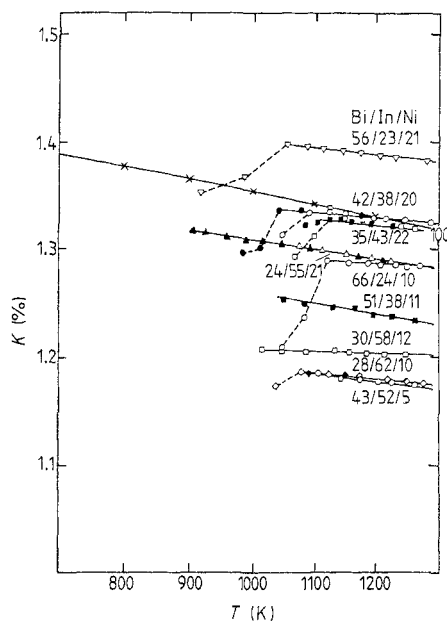
Figure 3. Knight shift K for ^{209}Bi in liquid Bi–In–Ni alloys: $\times$, pure Bi.

$d(\Delta B)/dT < 0$ [28, 29] and hence $\Delta B_Q \simeq 1$ G. R_Q increases markedly at intermediate c in the liquid Bi–In alloy (to about 4 G). This case has been discussed in [9], where a concentration of about 10% of BiIn associates was estimated at $c_{Bi} = 0.50$. In In–Ni, associations may be suspected in the present systems, introducing an additional linewidth; however, at low concentrations of the association partner (here c_{Ni}/c_{In}), quadrupolar linewidths are observed to remain small [9].

## 3. Experimental results for Bi–In–Ni systems

3.1. Spectrometer

The measurements were performed using the high-temperature, high-field, CW NMR spectrometer described earlier [30]. After a 37 Hz lock-in amplifier, the signals were digitised and several sweeps accumulated to 'packets' in a small computer.

The field used was usually 4.0 T and was checked by D_2O resonance; the sweep was sawtooth ±25 G with a period of typically 2 min. Typical measuring times per point (c, T fixed) were between 10 and 20 h, split into 10 min 'packets'.

The samples were contained in quartz cells 0.7 cm in diameter by 1.3 cm long, and wrapped with a RF coil of about five windings (QF = 30). The heater was a bifilar winding on a sintered Al_2O_3 (Alsint) tube. The temperature was measured at the sample with a Pt–(Pt–Rh) thermocouple; the temperature was stable and known to within about ±3 K. The RF coil, heater winding and thermocouple were bonded using high-temperature cement.
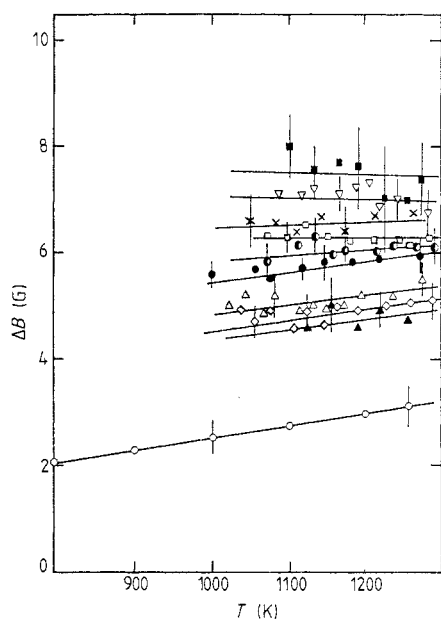
Figure 4. Linewidth ΔB for ^{115}In in Bi–In–Ni alloys in the liquid state: ——, lines drawn through experimental points; $\bigcirc$, 100 at.% In; $\blacktriangle$, $In_{52}Bi_{43}Ni_5$; $\diamondsuit$, $In_{62}Bi_{28}Ni_{10}$; $\times$, $In_{38}Bi_{51}Ni_{11}$; $\bullet$, $In_{58}Bi_{30}Ni_{12}$; $\triangle$, $In_{24}Bi_{66}Ni_{10}$; $\mathbb{O}$, $In_{38}Bi_{42}Ni_{20}$; $\triangledown$, $In_{23}Bi_{56}Ni_{21}$; $\square$, $In_{43}Bi_{35}Ni_{22}$; $\blacksquare$, $In_{55}Bi_{24}Ni_{21}$.
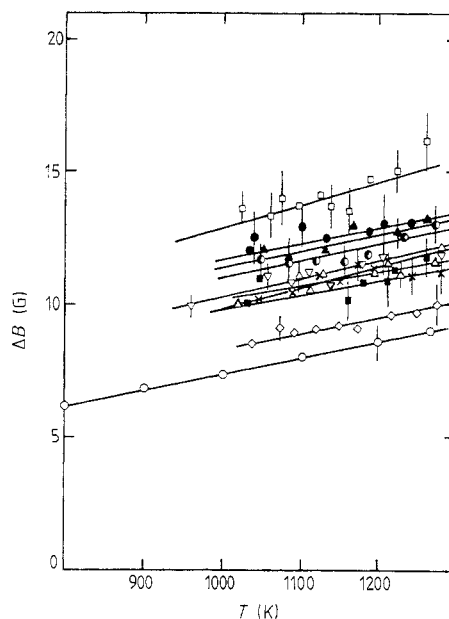
Figure 5. Linewidth ΔB for ^{209}Bi in Bi–In–Ni alloys in the liquid state: $\bigcirc$, 100 at.% Bi; $\blacksquare$, $Bi_{43}In_{52}Ni_5$; $\triangle$, $Bi_{66}In_{24}Ni_{10}$; $\blacktriangle$, $Bi_{51}In_{39}Ni_{10}$; $\diamondsuit$, $Bi_{28}In_{62}Ni_{10}$; $\bullet$, $Bi_{30}In_{58}Ni_{12}$; $\triangledown$, $Bi_{56}In_{23}Ni_{21}$; $\times$, $Bi_{42}In_{38}Ni_{20}$; $\mathbb{O}$, $Bi_{24}In_{55}Ni_{21}$; $\square$, $Bi_{35}In_{43}Ni_{22}$.

3.2. Samples

Samples were produced from 99.999% pure materials Bi, In and Ni (Ventron) by weighing (to 5 mg in 8 g total mass) into quartz ampoules, degassing and sealing. Each ampoule was then kept for 2 weeks at 1440 K; for cooling it was rapidly dipped into water. The ingot was roughly cut and then ground in an achate mortar at about 70 K. By sieving, particles of diameter 40 μm or less were selected. About 0.6 g of this sample material was mixed with 70 vol.% of Al_2O_3 powder (purity, 99.999%) of similar grain size; the mixture was degassed in the sample cell again at 750 K and 10^{-6} Torr and was then sealed.

The sample compositions were determined by plasma spectroscopy from 0.1 g amounts of the powdered material; deviations from nominal compositions were about 5% or less. In the results and discussion, each sample is quoted under its measured composition rounded to the nearest 1% for simplicity.

3.3. Results

The NMR signals for ^{115}In and ^{209}Bi showed signal-to-noise ratios of about 10 at the higher Ni concentrations. The signals were symmetrical within error limits. The Knight shifts K were determined from zero crossing and corrected for RC of the lock-in amplifier; the linewidths ΔB were taken as the distance between positive and negative peak. Since the modulation amplitude was kept below two thirds of the linewidth, the modulation
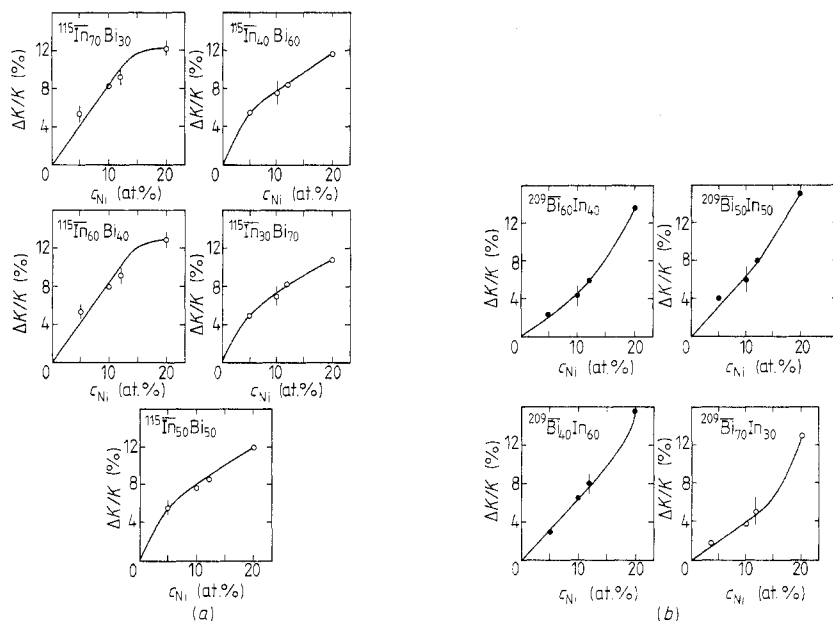
Figure 6. (*a*) Fractional change in Knight shift for ^{115}In in liquid Bi–In–Ni alloys, at 1200 K, as functions of Ni concentration. The curve for $c_{Ni} = 0$ is extrapolated from data given in [7]. Curves are drawn to guide the eye. (*b*) Fractional change in Knight shift for ^{209}Bi in liquid Bi–In–Ni alloys, at 1200 K.

correction could be neglected. Uncertainties in the Knight shifts were $2 \times 10^{-4}\%$ from ΔB_0, $5 \times 10^{-5}\%$ from frequency and sweep calibration; the scatter in the points gives $\delta K \lesssim 10^{-3}\%$, and $\delta(\Delta B) \lesssim 1$ G.

Figures 2 and 3 show the measured Knight shifts for In and Bi. The Knight shifts increase with increasing Ni concentration and decrease with increasing temperature. The addition of Bi to In raises the ^{115}In (In to Bi reduces the ^{209}Bi) shift.

In figures 4 and 5, we present the linewidths for ^{115}In and ^{209}Bi, which increase with increasing temperature (except for $c_{Ni} = 0.20$). The absolute values are raised by a factor of up to 3 for In (and up to 2 for Bi).

In figure 6 the Knight shifts are presented as curves against the Ni concentration. Note here that the experimental error in K is about the same as the uncertainty in K introduced by the error margin of the concentration values. Figure 7 shows the concentration dependence of K at 1200 K. For comparison, the Knight shifts of the binary Bi–In systems from [8] have been extrapolated to the same temperature.

4. Discussion

4.1. *K in Bi–In–Ni against concentration*

The results presented in figures 2 and 3 present an extensive study of the influence of a d element solute on a liquid alloy matrix A–B, when there is a clear bonding tendency in the A–B system. Unfortunately, no susceptibility or conductivity data yet exist for the ternary system, and in fact the K–χ relation may be expected to be of a similarly complicated form to that for Bi–In.
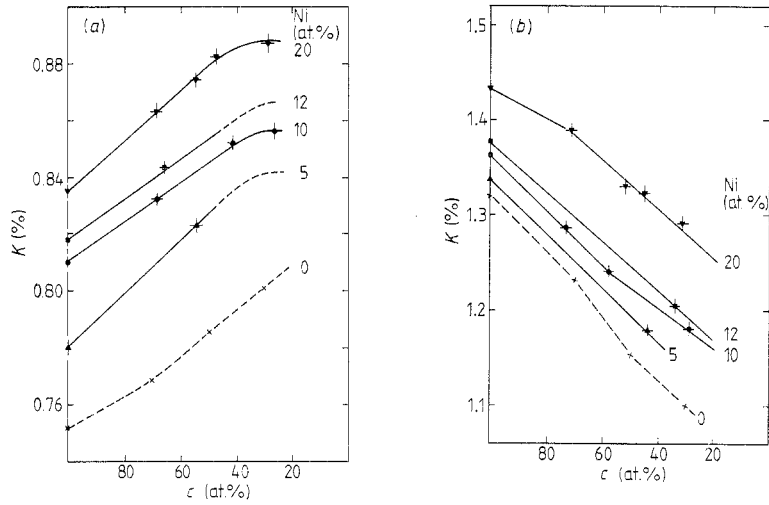
Figure 7. (*a*) Change of Knight shift for [115]In in liquid Bi–In–Ni alloys at 1200 K; $c = c_{In}/(c_{In} + c_{Bi})$. (*b*) Change in Knight shift for [209]Bi in liquid Bi–In–Ni alloys at 1200 K; $c = c_{Bi}/(c_{In} + c_{Bi})$.

The change in K on the addition of a concentration c_i of Ni, referred to $K(j)$ in the alloy $Bi_{1-x}In_x$, is presented in figure 6. It is customary to introduce

$$\Gamma_{ij} = (1/c_i)[\Delta K(j; c_i)/K(j; c_i = 0)] \tag{7}$$

which is larger for $j \equiv$ In than for $j \equiv$ Bi, but it decreases with increasing c_{Ni} for In, while it increases for Bi.

One phenomenological *ansatz* for Γ is based on the concept of electron spin density polarisations used in [31, 32]. Let an atomic 3d cell i acquire an average magnetic moment by the external field B_0, either by aligning 'local moments' (permanent ones), or by polarising a high local density of states ('no local moment'). The resulting effect on a neighbouring matrix atom j at r_{ij} can be described by the induced change $s_{ij}(r_{ij})$ in electron spin density [31, 32] which averages over the position of i to $s_j = \langle s_{ij}(r_{ij}) \rangle_i$. Compared with the Knight shift K without the d atoms, and with the corresponding spin polarisation s_p, one has a change

$$\Delta K/K = (s_j - s_p)/s_p \tag{8}$$

where in the free-electron picture $s_p = \chi_s \Omega P$. If one now assumes that only the nearest

Table 2. Spin-density polarisation $\Delta s_j/s_j$ for $j \equiv$ Bi, In in liquid Bi–In–Ni alloys at $c_{Ni} = 0.10$ and $T = 1200$ K. Interpolated values at rounded c_{Bi}/c_{In} are given. The lower set describes binary liquid Bi–In at $T = 770$ K; data from [8] ($c_{Ni} = 0$).

Bi	0	27	36	45	54	63	90
In	90	63	54	45	36	27	0
$(\Delta s/s)_{Bi}$	—	0.06	0.053	0.048	0.035	0.031	0.026
$(\Delta s/s)_{In}$	0.064	0.068	0.065	0.063	0.062	0.058	
Bi	0	30	40	50	60	70	100
In	100	70	60	50	40	30	0
$(\Delta s/s)_{Bi}$	—	−0.020	−0.021	−0.021	−0.020	−0.018	—
$(\Delta s/s)_{In}$	—	0.008	0.010	0.010	0.009	0.008	—

neighbours (effectively about 12) contribute and that there is no preferred arrangement i–j (nearest-neighbour distance $\bar{r}_{ij}$), then

$$(\Delta s/s)_j = [\Delta s(\bar{r}_{ij})]/s_p \simeq \tfrac{1}{12}\Gamma_j \qquad \text{for given } i. \tag{9}$$

For In and Sb in liquid $In_{1-x}Sb_x$, $(\Delta s/s)_{In} = +0.022$ and $(\Delta s/s)_{Sb} = -0.014$ were obtained in [33]. Similarly it follows for Bi in Bi–In [8] that $(\Delta s/s)_{Bi} < 0$, while $(\Delta s/s)_{In} > 0$. The negative signs for Sb and Bi are probably caused by the p character at ε_F.

For In and Bi in Bi–In–Ni, the results are presented in table 2. It should be realised that $\Delta s/s$ contains the effect on both terms K_{Nis} and K_{Nid} in equation (4); the shapes of the curves in figure 6 are presumably due to their interplay in the quadratic and linear terms in c_{Ni}. Note that $\Delta s/s$ is generally positive for $c_{Ni} = 0.10$; it decreases somewhat for In upon alloying Bi but increases for Bi upon alloying In. The last observation suggests a connection with $\Delta s/s < 0$ for Sb and Bi [8, 33]. The large change observed— a factor of 2 in $(\Delta s/s)_{Bi}$ by adding In—is in itself a characteristic effect of the binary Bi–In alloy; pictorially it may be thought of either as a 'mixing' of the (larger) In spin polarisation, $(\Delta s/s)_{In} = 0.064$, into the smaller value of Bi, $(\Delta s/s)_{Bi} = 0.026$, via the bonding Bi–In interaction or as a consequence of the increase in $N(\varepsilon_F)$.

When comparing the present results with those of the Cu–Ga–Mn system (2 at.% Mn; local moment at Mn) [10], one notices much smaller spin polarisations in table 2 than there ($(\Delta s/s)_{Cu}$ between -0.35 and -1.6; $(\Delta s/s)_{Ga}$ between -0.22 and $+0.2$). We suspect that this is due to the localised moment, perhaps together with electron configurations on Cu and Ga which are more favourable to an overlap with the 3d impurity.

We turn now to the dependence of $K(Bi)$ and $K(In)$ on c_{Bi}/c_{In} (figure 7). The general shape is virtually independent of c_{Ni}, including the characteristic bend-over from slope to plateau at $c_{Bi}/c_{In} \simeq 1.5$ known from the results in [8] obtained at lower temperatures.

Since the changes in K due to alloying Bi–In, and on further addition of Ni are small ($\Delta K/K \lesssim 10^{-1}$), it is natural to try an expansion *ansatz*. At a fixed temperature and for Bi, say, one calculates

$$K(c_{Bi}/c_{In}/c_{Ni}) = K(1/0/0) + (\Delta K/\Delta c_{In})c_{In} + (\Delta K/\Delta c_{Ni})c_{Ni} \tag{10a}$$

$$\Delta K/\Delta c_{In} = [K(1 - c_{In}/c_{In}/0) - K(1/0/0)]/c_{In} \tag{10b}$$

Table 3. Comparison of K as measured on Bi and In, with values calculated from the expansion *ansatz* equation (10a). $T = 1200$ K.

Ni (at.%)	Bi (at.%)	In (at.%)	K_{exp} (%)	$K(c = 1)$ (%)	ΔK_{Bi-In} (%)	ΔK_{Bi-Ni} (%)	K_{calc} (%)
				$K(Bi)$			
5	66.5	28.5	1.250	1.320	-0.091	$+0.021$	1.250
10	64	26	1.276	1.320	-0.091	$+0.050$	1.279
20	59	21	1.380	1.320	-0.091	$+0.150$	1.379
5	47.5	47.5	1.194	1.320	-0.145	$+0.021$	1.196
10	45	45	1.223	1.320	-0.145	$+0.050$	1.225
20	40	40	1.330	1.320	-0.145	$+0.150$	1.325
				$K(In)$			
5	28.5	66.5	0.806	0.752	$+0.021$	$+0.033$	0.806
10	26	64	0.832	0.752	$+0.021$	$+0.053$	0.826
20	40	40	0.863	0.752	$+0.021$	$+0.075$	0.848
5	47.5	47.5	0.825	0.752	0.040	0.033	0.825
10	45	45	0.845	0.752	0.040	0.053	0.845
20	45	45	0.880	0.752	0.040	0.075	0.867

etc. For the terms $\Delta K = (\Delta K/\Delta c)\,c$ the real changes were taken from the binaries [2, 3, 8] at the actual concentration of the respective alloy partner (e.g. for Bi/In/Ni = 66/24/10, K on In; $\Delta K/\Delta c_{In}$ at $c_{In} = 0.24$ in Bi–In, and $\Delta K/\Delta c_{Ni}$ at $c_{Ni} = 0.10$ in In–Ni). In table 3 we show these results. Interpolation has been used to refer the actual K-values at measured concentrations to nominal concentrations.

If the In–Bi interaction has an effect on the shift induced by Ni on Bi (or In), the shifts K_{calc} calculated from equation (10a) will not agree with the observed value K_{exp}. This is indeed the case for $K(\text{In})$—$c_{Ni} = 0.10$, $c_{Bi} = 0.26$ and $c_{Ni} = 0.20$, $c_{Bi} = 0.40$—but not for $K(\text{Bi})$. The In–Bi alloying appears to influence only that term in the change of K induced by Ni which is quadratic in c_{Ni}.

4.2. K in Bi–In–Ni against temperature

In table 4, we present dK/dT for Bi and In for the various concentrations studied. Again trends known from the binary systems survive, such as, for In, the In matrix trend $dK/dT < 0$ dominates until $c_{Ni} \geqslant 0.20$. Note, however, that, for Bi, $|dK(\text{Bi})/dT|$ is always smaller than in pure Bi–Ni (see table 1); this might be connected with the reason for the larger change in $\Delta s_{Bi}/s_{Bi}$, compared with $\Delta s_{In}/s_{In}$, i.e. the 'mixing in' of In properties.

Table 4. Temperature dependence dK/dT for liquid Bi–In–Ni alloys. Derivatives were determined from 1080 to 1280 K. The estimated uncertainty is about $\pm 1 \times 10^{-7}\,\text{K}^{-1}$. The $\text{Bi}_{50}\text{In}_{50}$ values are from [8]. $T = 579$–770 K.

Ni (at.%)	Bi (at.%)	In (at.%)	$dK(\text{Bi})/dT$ $(10^{-7}\,\text{K}^{-1})$	$dK(\text{In})/dT$ $(10^{-7}\,\text{K}^{-1})$
5	43	52	−7	−6
10	28	62	−5.5	−5.5
12	30	58	−2	−4.5
11	51	38	−9	−5
10	66	24	−3	−5
21	24	55	−9	−0.5
22	35	43	−6.5	+0.5
20	42	38	−4.5	0
21	56	23	−7	+2
0	0	100	./.	−6.8
0	100	0	−12	./.
0	50	50	−4.7	−9.4

4.3. Linewidths

The linewidths for In (figure 4) may be described as showing a general increase with increasing c_{Ni} and, within that increase, considerable variation with c_{Bi}/c_{In}. There is striking parallelism between d/dT of $K(\text{In})$ and $\Delta B(\text{In})$, (figures 2 and 4) as one adds Ni to In. It is tempting to search here for an influence of Bi–In bonding. However, in view of the systematic uncertainties that are apparent between sets for almost the same compositions (such as $\text{Bi}_{28}\text{In}_{62}\text{Ni}_{10}$ and $\text{Bi}_{30}\text{In}_{58}\text{Ni}_{12}$, where the differences may have been caused by sample quality, inhomogeneity of composition, signal-to-noise ratio, etc), it appears impossible to infer conclusions from the variation with c_{Bi}/c_{In}. For Bi in the Bi–In system, the linewidth increase due to quadrupolar interaction is considerable at 400–800 K [34]. The widths $\Delta B(\text{Bi})$ for Bi–In–Ni (figure 5) show comparable increases due to added Ni at $T \geqslant 1000$ K. Again possible variations in $\Delta B(\text{Bi})$, which would be expected to be smooth in c_{Bi}/c_{In}, are not unambiguously recognisable.

5. Conclusion

In the ternary liquid alloys Bi–In–Ni, we have studied the simultaneous effects of alloying a III–V pair and of the addition of a 3d impurity. The Knight shifts as well as the linewidths change considerably; however, these changes are of similar size to the changes observed for the binaries Bi–In, Bi–Ni and In–Ni. This is not trivial because non-linear effects are obvious in K, first for Bi and In in Bi–In [8] (the slope and plateau shape). This effect is in good agreement with the association model as formulated in [9]. Looking at the Bi Knight shift as a function of c_{In} in the binary liquid alloy Bi–In [8], K(Bi) first displays a roughly linear slope and then bends over to a constant plateau. In the association model, this is the shape of the curve 'probability of a Bi atom to be part of an associate BiIn, as a function of c_{In}'. (Note that ΔB_Q(Bi) shows a maximum at intermediate concentrations because the exchange process makes the plateau bend down again towards $c_{Bi} = 0$.) The situation is symmetric for c_{In} and K(In). Secondly, there are terms proportional to c_{Ni}^2 for K(Bi) and K(In) in Bi–Ni and In–Ni owing to an increase in effective Ni cell moment by pairing. The linewidths prove that the quadratic term fluctuates independently of the linear term; both terms add for K(Bi) but oppose each other for K(In).

Calculations of induced hyperfine fields for polyvalent atoms in liquid alloys would be of great help. Since additivity is almost obeyed, in the present system at least, a perturbation *ansatz* may work.

The similarity of results for K against c for Bi–In [8] and Bi–Tl [23], the magnitude and sign of K for liquid p metals and alloys, and the general tendency $dK/dc_{3d} > 0$ all point to the usefulness of the basic *ansatz* equation (1), which is based on conduction electrons with local s character at ε_F. This is an apparent contradiction to the prevalence of p character suggested by the recent precise UPS and XPS results for liquid p metals in [17]. It is hoped that the present results can help towards elucidation of these questions, once a good model and/or calculation is offered for the electronic properties of liquid s, p and d metal alloys.

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